MPA MaterialsMatter

June 2011

INSIDE

Jennifer Hollingsworth

Connecting the dots through collaboration

By Francisco Ojeda
ADEPS Communications

The Center for Integrated Nanotechnologies (CINT) offers scientists access to world-class facilities and advanced tools that enables nanoscience discoveries.

However, it is not CINT's capabilities that make it special, said Jennifer Hollingsworth; instead, it's the national user facility's collaborative environment.

"You combine the capabilities and the researchers at CINT and you have breakthrough research happening here," said Hollingsworth (MPA-CINT). "It's a good model for doing interdisciplinary science."

Collaboration and integration are central to CINT. Teaming with external users is at the core of the user facility's mission and developing the principles that govern the integration of nanoscale materials is at the heart of its vision.

Hollingsworth herself embodies the sort of cross-disciplinary expertise required in nanoscience. Originally trained as a classical inorganic chemist with a materials science inclination, she is now well versed in the science and language of her physicist and biologist collaborators. As a CINT scientist, she supports the center's nanophotonics and optical nanomaterials science thrust and is the Los Alamos lead for its nanowires integration focus area.

Hollingsworth joined the Laboratory's Chemistry Division in 1999 as a Director's-funded Postdoctoral Fellow after earning her PhD in inorganic chemistry from Missouri's Washington University in St. Louis.

"She is really enthusiastic and energetic so that makes her fun to work with," said CINT Chief Scientist Tom Picraux. "She is very important to CINT because she adds the

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From David's Desk

The Materials Capability Review was held the first week of this month. Several people from MPA Division were either featured as speakers or gave posters. We wanted to thank them for their effort. It takes time to do this well, and I was pleased with the result.

The review began with a charge to the committee given by Duncan McBranch and Susan Seestrom, who has overall responsibility for the materials capability. Wendy Cieslak gave a presentation summarizing the materials capability across the Laboratory, followed by Toni Taylor who spoke on the implementation plan for our materials strategy. This implementation plan came out of the deep dives that involved people from across the materials community at LANL, including numerous MPA personnel. This input was critical to advancing the implementation plan, and hopefully Toni will have an opportunity in the near future to discuss this at an all-hands meeting for MPA Division.

We have structured the MCR around the three primary themes of the materials strategy: defects and interfaces, emergent phenomena, and extreme environments. We also try to cover actinide materials and a major facility in each review. This year, we used radiation damage as a topical area for extreme environments, nuclear energy as a topical area for defects and interfaces as well as to cover actinide research, and materials for clean energy applications as a topic for emergent phenomena. We also had an overview and tour of the LANSCE facility stressing materials research and looking forward to the Materials Test Station for radiation damage and to MaRIE.

The verbal out-brief of the committee was very positive on the quality of the research presented in the technical sessions. Several MPA presentations were called out as particularly notable for the progress that has been made. In the energy session I chaired, Rod Borup spoke about the fuel cell program, backed up by a couple of posters. The committee clearly appreciated the quality of the fuel cell effort. There was a keen appreciation of the creativity and depth needed in use-inspired research on catalysts and membrane materials to obtain the performance characteristics necessary for practical implementation of fuel cell technology. We also had posters in this session on hydrogen storage and applied superconductivity that were recognized for the quality and productivity of the research effort.

". . . we provided the committee with strong evidence of the quality and technical relevance of our research efforts."

In the session on materials in radiation environments, Amit Misra stepped in at the last minute for Mike Nastasi and gave a good overview of the work being carried out in the Energy Frontier Research Center on Materials at Irradiation and Mechanical Extremes. In this review, we featured both EFRCs, with Victor Klimov presenting on the Center for Advanced Solar Photophysics.

Overall, the technical presentations were well received and we provided the committee with strong evidence of the quality and technical relevance of our research efforts. We appreciate the efforts of all of our staff that gave presentations or posters and contributed to making the review of the materials research effort a success. We also want to thank Jean Sanzo for her work on organizing the review and Karen Kippen and the communications team for all their efforts in support of the review.

The *MST e-News* newsletter has pictures from the review, and I encourage you to peruse that to get a better feeling for the event.

—MPA Deputy Division Leader David Watkins

Hollingsworth . . . chemical synthesis of nanomaterials aspect that we count on for our studies. She's also a good collaborator because she does her homework and understands things that are needed for the project."

As part of her CINT research, Hollingsworth recently collaborated with Laboratory scientists to develop a new class of nanocrystal quantum dots (NQDs) that benefit research ranging from bioimaging to solid-state lighting.

NQDs are semiconductor nanoparticles with remarkable size-tunable optical properties, including the ability to efficiently emit light. Compared with molecular dye fluorophores, optically excited NQDs are more stable. However, NQD applications have been limited due to a property known as fluorescence intermittency, or blinking.

Under continuous illumination, single nanocrystal quantum dots turn "on" and "off" in an unpredictable fashion. Blinking limits the utility of conventional NQDs for applications requiring continuous and reliable emission of photons, such as single-particle tracking in advanced bioimaging and as single-photon light sources in quantum cryptography.

Hollingsworth and her team applied an ultrathick and structurally perfect shell of a higher bandgap semiconductor to the core NQD to create giant NQDs, which have suppressed blinking and remarkable photostability. The ability to follow the trajectory of single molecules as they perform their biological functions is an important goal for advanced bioimaging.

"Without her, the project would not have been possible," said collaborator Han Htoon (Physical Chemistry and Applied Spectroscopy, C-PCS), who has worked with Hollingsworth for 10 years. "She and her postdocs created the inorganic shell that helped stop the blinking. Her expertise in this area is invaluable."

Since this discovery, Hollingsworth has begun collaborating with external researchers interested in capitalizing on the new properties of these nanomaterials and enhancing them by combining them with other nanoscale structures, such as plasmonic nanoparticles. The work, which supports the Laboratory's national energy security efforts, recently received a patent.

Hollingsworth and Htoon are also co-principal investigators on a project exploring the use of giant NQDs for high-efficiency solid-state lighting. Their work has received a Single-Investigator and Small-Group Research (SISGR) project grant from the Department of Energy's Office of Science, Basic Energy Science.

Jennifer Hollingsworth's favorite experiment

What: Catalyzed growth of metastable indium sulfide layered phase

Where: Washington University in St. Louis. Professor Bill Buhro's materials inorganic chemistry laboratory

When: 1998

Why: We were exploring approaches for circumventing energy barriers to crystal growth in covalent, non-molecular solids.

How: Typically, high temperatures are required to synthesize crystalline forms of these materials (>400 °C), and the resulting crystal structures are lowest-energy, thermodynamic phases. In contrast, metastable (higher energy) phases are common in the case of molecular solids for which a range of catalyzed-growth strategies are known that lead to kinetic control of the reaction, production of metastable structures, and significant structural diversity. We found that certain molecular additives (e.g., benzenethiol) could catalyze the low-temperature (203 °C) growth of crystalline indium sulfide (InS) and indium selenide (InSe). Furthermore, the resulting InS phase was a new crystalline structure that had not been observed previously.

The a-ha moment: The question we had was whether the new InS phase was a "metastable" structure. To establish that the new, pseudographitic structure was truly less stable than the known InS crystalline phase, we subjected it to thermal annealing at high temperatures (>400 °C), which caused it to transform to the known phase. In addition, we found that we could achieve the same transformation at lower temperatures (203 °C) using a "recrystallization catalyst" in the form of molten indium metal. The molten flux dissolved the nanocrystalline metastable material and effected the recrystallization of the known, now clearly more stable, thermodynamic phase, but at half the temperature required for solid-state recrystallization.

Resonance-stabilized anion exchange polymer electrolytes

In research aimed at improving the performance of alkaline membrane fuel cells, researchers Yu Seung Kim and Dae Sik Kim (Sensors and Electrochemical Devices, MPA-11) and Andrea Labouria (Polymers and Coatings, MST-7) have developed advanced electrode materials based on guanidinium cation and

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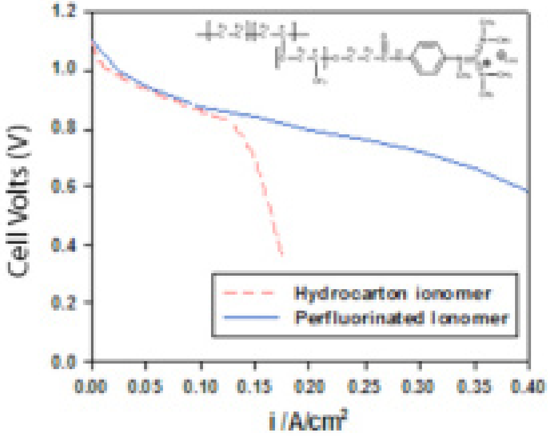

H_2/O_2 alkaline fuel cell performance at 60°C.

Resonance . . . perfluorinated polymers.

Traditional tetra-alkyl ammonium based hydrocarbon ionomers suffered from their low reactant permeability and incompatibility with electro-catalysts. Perfluorinated polymer electrolytes have been known for their excellent gas permeability and have been used for the electrode materials in proton exchange membrane fuel cells. However, the cation functional groups tethered in perfluorinated system become extremely unstable under alkaline conditions, which limited their use in alkaline fuel cells.

In order to improve the cation stability, the researchers inserted an electron donating spacer between perfluorinated side chain and cations, which increased electron density of the cations and thus stabilized the cations. In addition, they used a high basic guanidinium functional group, which formed a stable resonance structure, instead of a tetra alkylammonium functional group. The novel perfluorinated ionomer showed excellent stability under pH conditions with reasonably high hydroxide conductivities.

The researchers found that alkaline fuel cell performance using the perfluorinated polymers as electrode materials significantly improved (see figure).

The research, which is part of the Laboratory's energy security mission, was funded by the DOE/EERE/Fuel Cell Technologies Program.

Nanolayered composites suppress irradiation hardening

A major issue with structural metals in nuclear power reactors is the hardening and embrittlement caused by the accumulation of radiation-induced defect clusters.

In research appearing in *Scripta Materialia*, Center for Materials at Radiation and Mechanical Extremes researchers discovered that nanolayered composites containing interfaces that attract, absorb and annihilate point defects suppress the formation of defect clusters and hence, the radiation-induced hardening.

The researchers used focused-ion-beam machined compression specimens to investigate the effect of ion irradiation on the strength and deformability of sputter-deposited copper and copper/niobium multilayers with different layer thickness.

They found that the flow strength of films increased by more than a factor of 2 due to radiation damage but in multilayers, the magnitude of radiation hardening decreased with decreasing layer thickness. When the layer thickness decreases to 2.5 nm, insignificant hardening and no measurable loss in deformability is observed after implantation.

In the future, the researchers plan to investigate the properties of ion irradiated nanolayered composites for different loading conditions, other than compression used in this study.

This work is sponsored by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Energy Frontier Research Center. The high-dose helium ion implantation work is supported by LANL-LDRD. Nanoindentation was performed, through an approved user project, at the Center for Integrated Nanotechnologies, a DOE-BES sponsored national user facility.

Reference: "Compressive flow behavior of Cu thin films and Cu/Nb multilayers containing nanometer-scale helium bubbles," by Nan Li, Nathan Mara (MPA-CINT), Yongquiang Wang (Structure/Property Relations, MST-8), Michael Nastasi and Amit Misra (MPA-CINT), *Scripta Materialia* **64**, 974–977 (2011).

Technical contact: Amit Misra

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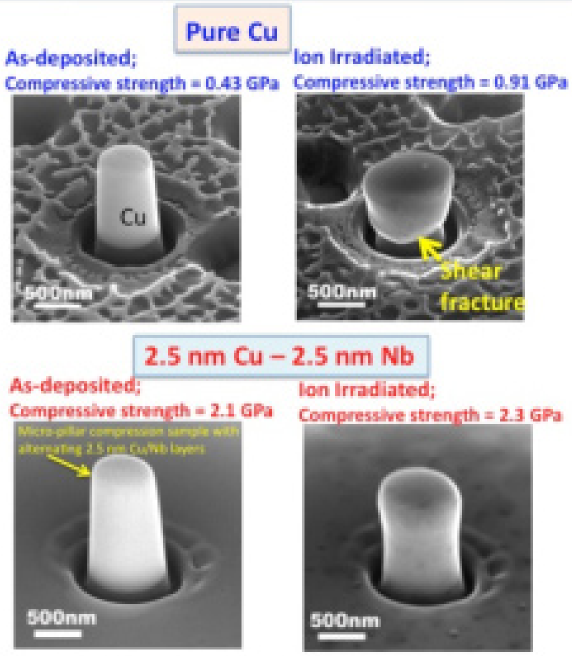
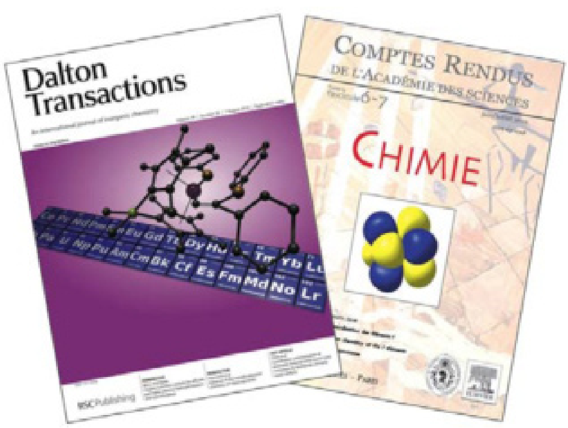


Example shows micro-pillar compression tests (performed in CINT) on pure Cu and 2.5 nm Cu-Nb multilayers. After helium ion irradiation, Cu hardens by more than a factor of two and loses deformability. The nanolayered Cu-Nb shows insignificant hardening and no loss in deformability.

MPA chemists invited to contribute to two international journals devoted to high-impact actinide science



In recognition of the broad-ranging significance and impact of f-element chemistry, two international journals, *Dalton Transactions* and *Comptes Rendus Chimie*, recently devoted issues to actinide chemistry. These themed issues contain contributions from leaders in the area from all over the world, and encompassed a wide range of new developments in f-element chemistry. As leaders in actinide chemistry, MPA-MC chemists Jaqueline L. Kiplinger and James M. Boncella (both of Materials Chemistry, MPA-MC) were invited to contribute to the high-profile issues. Both reported new actinide chemistry and brought enhanced visibility to Los Alamos. Kiplinger's co-workers on the papers *(Dalton Trans*. **39**, 6826-6831, 2010; *C. R. Chimie* **13**, 790-802, 2010) include Robert K. Thomson (Seaborg Postdoctoral Fellow), Christopher R. Graves (former Seaborg Postdoctoral Fellow), Brian L. Scott (MPA-MC) and David E. Morris (MPA-CINT) and Boncella's co-workers on the papers (*Dalton Trans.* **39**, 6841-6846, 2010; *C. R. Chimie* **13**, 758-766, 2010) included Douglas L. Swartz (former visiting graduate student), Liam P. Spencer (former Seaborg Postdoctoral Fellow), Ping Yang (former Seaborg Postdoctoral Fellow, Physics and Chemistry of Materials, T-1), Enrique R. Batista (T-1), Brian L. Scott, and Aaron L. Odom (Michigan State University). The research was supported by the DOE Office of Science-Heavy Element Chemistry Program, LANL LDRD program, and through the LANL G.T. Seaborg Institute.

Technical contacts: Jaqueline L. Kiplinger, James M. Boncella

Laboratory's materials physics researchers give invited talks at American Physical Society meeting

In addition to many contributed talks, MPA researchers gave six invited presentations at the American Physical Society's March meeting in Dallas.

In "Active Terahertz Metamaterial," Toni Taylor (MPA-DO) presented a series of novel THz metamaterials and showed that their resonant response can be controlled using optical or electrical excitation and thermal tuning. This tuning ability potentially enables the creation of efficient THz devices with numerous sensing, imaging, and diagnostic applications. Her co-authors were Houtong Chen, John O'Hara, Abul Azad, Jiangfeng Zhou, Ranjan Singh, Matthew Reiten, and Dibakar Chowdhury (all MPA-CINT). The work is supported by LANL-LDRD and BES/CINT user facility funding.

In " 'Listening' to the spin noise of electrons and holes in semiconductor quantum dots," Scott Crooker (Condensed Matter and Magnet Science, MPA-CMMS) described measuring electron and hole spin dynamics in semiconductors through the use of a spin noise spectrometer to passively "listen" to small spin noise signals. The work, in collaboration with Yan Li, D. Smith, J. Brandt, C. Sandfort, A. Greilich, D. Reuter, A. Wieck, D. Yakovlev and M. Bayer, suggests possible routes towards non-perturbative, sourceless magnetic resonance of few-spin systems. The work is supported by the LANL LDRD program.

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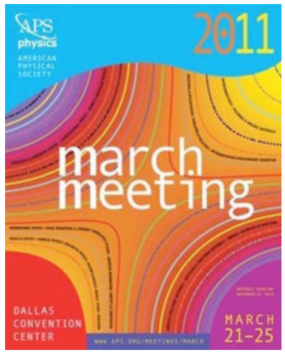
Talks . . . In “Understanding anisotropy to develop superconducting design principles,” Filip Ronning (MPA-CMMS) described attempts to understand the role of reduced dimensionality and increased bandwidth within the “115” class of heavy fermion superconductors by examining trends in the charge and spin degrees of freedom that are correlated with superconductivity. The work, in collaboration with Eric Bauer, Paul Tobash, Moaz Altarawneh, Hironori Sakai, Kris Gofryk, Neil Harrison, and Joe Thompson, (MPA-CMMS), Jian-Xin Zhu (Physics of Condensed Matter and Complex Systems, T-4), HB Rhee and Warren Pickett (University of California, Davis), aims to lay the foundation for a modern, microscopic version of Matthias’ rules for unconventional superconductivity from which superconducting design principles can be developed. The work is supported by LANL-LDRD.



In “Ce115’s and beyond,” Joe Thompson (MPA-CMMS) discussed recent studies on the Ce115 family of heavy-fermion materials showing that characteristics of magnetism and superconductivity in these 4f- and 5f-electron systems bear similarities to those in cuprate and iron-pnictide superconductors. His collaborators include Eric Bauer, A. Bianchi, K. Grube, Z. Fisk, M. Kenzelmann, H. O. Lee, R. Movshovich, M. Nicklas, T. Park, F. Ronning, H. Sakai, V. A. Sidorov, O. Stockert, H. v. Lohneyson, and H. Yasuoka. Work at Los Alamos is performed under the auspices of the Department of Energy Office of Basic Energy Sciences.

In “Universal Signatures of Metamagnetic Quantum Criticality,” Franziska Weickert (MPA-CMMS) discussed the qualitative features of a field-driven quantum critical end-point and presented real examples of metamagnetic systems, where the characteristics can be found experimentally. Co-authors included P. Gegenwart, M. Garst, and F. Steglich and the work is supported by the Max-Planck Institute for Chemical Physics of Solids and the LANL LDRD program.

In “Bose-Einstein Condensation and Asymmetry induced by Quantum Fluctuations in $NiCl_2$-$4SC(NH_2)_2$,” Vivien Zapf (MPA-CMMS) reviewed Bose- Einstein condensation (BEC) in quantum magnets and presented magnetization, thermal conductivity, and specific heat data to probe BEC, in particular the effect of quantum fluctuations on the boson mass. Co-authors include Y. Kohama, M. Jaime, C. Batista, K. Al-Hassanieh, A. Chernyshev, P. Sengupta, A. Sologubenko, J. Mydosh, A. Paduan-Filho, and S. Gangadharaiah. The work is supported by the National Science Foundation, the DOE and the state of Florida, as well as the LANL LDRD program and the Brazillian agency CNPq.

HeadsUP!

Review foreign nationals host and co-host responsibilities

Hosts of foreign nationals should regularly review the list of responsibilities to ensure that they stay in compliance with DOE and LANL policies. See host and co-host responsibilities at int.lanl.gov/securityisec/fva/hosts.shtml. Contact OCI/FV&A at 665-1572 or 665-5561 if you have questions or concerns about your obligations as a responsible host or co-host.

Celebrating service

Congratulations to the following MPA employees celebrating service anniversaries this month:

Paul Mombourquette, MPA-11	20 years
Eric Brosha, MPA-11	20 years

MPA MaterialsMatter

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To submit news items or for more information,
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To read past issues see
www.lanl.gov/orgs/mpa/materialsmatter.shtml

Los Alamos NATIONAL LABORATORY EST.1943

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The Superconductivity Technology Center works to develop energy efficient technologies in collaboration with industry and universities and in support of the LANL energy security mission. A stable core of the center for several years has focused on high temperature superconductor (HTS) materials for energy applications with funding from the DOE Office of Electricity Delivery and Energy Reliability (OE). The OE program includes both materials R&D and applications development, with scope ranging from fundamental studies of flux pinning to optimization of conductor properties for specific applications and into demonstrations of new applications concepts.

A related DOE Basic Energy Sciences (BES) program studies vortex matter across the range of superconducting materials with the aim of predicting, controlling, and designing the behavior of vortex matter in any superconductor. Also related is the work funded by DOE High Energy Physics (HEP) to understand and optimize HTS materials for very high field superconducting magnets. STC also has a growing portfolio of projects funded by and driven by the applications needs of the oil and gas industry; these projects include both more efficient conductors for well head and down hole power transmission and higher efficiency methods of separation of hydrocarbon impurities and waste products using RF power capabilities and expertise in the center.

" A stable core of the center for several years has focused on high temperature superconductor materials for energy applications..."

The STC pioneered the development of coated conductors–HTS tapes made using film coating of YBaCuO on thin metal substrates–which permit dramatically greater current densities than those in conventional copper cable, and enable new technologies to secure the national electric grid. Sustained world-class research including concept, demonstration, tech transfer and ongoing industrial support has moved this idea from the laboratory to the commercial marketplace. A focused effort on engineered nanoscale flux pinning defects combined with a push to thicker YBCO films has succeeded in increasing the critical current in coated conductors by a factor of 10 over the last 5 years. Another successful concept—elimination of electropolishing to achieve the 1-nm surface smoothness required of the metal substrate and replacement with solution deposition planarization, or SDP—won an R&D 100 award in 2010.

This technology has been sought out by multiple companies that manufacture coated conductors. In fact, much of the success achieved in improving critical current performance, reducing processing complexity and cost, and developing methods of long length characterization of tapes has been transferred to our industrial partners. Industrial partnerships remain a strong component of STC's efforts, and include seven current CRADAs and several additional ones under discussion.

STC has also demonstrated substantial innovation in applications using coated conductors. If you stop by the Los Alamos Research Park these days, as you walk west from the parking lot toward the building you will pass by the world's first overhead HTS cable. The enabling technology for this demonstration is a low-cost refrigeration system that uses no compressors, pumps, or moving parts. Based on a two phase distributed cooling method, pressurized liquid nitrogen flows through a small distribution tube, sprays out of orifices, boils in a vapor space surrounding the cable, and nitrogen vapor at or near 77 K flows down the surrounding commercial cryostat and exits. Using a few bar of distribution pressure, a temperature variation less than half a degree over the 100-foot length of cable has been demonstrated. No increase in temperature was observed when the HTS cable was energized with a 500 A dc current. Models show that the temperature variation in such a system over 10 miles would be only 2°K.

You might say STC is the victim of its own success, because based on these great strides OE has declared the development of coated conductors complete, and announced termination of this program in FY12. The talented and dedicated center staff are busy pursuing related energy programs from HEP, ARPA-E, DARPA and other sources. The BES vortex matter program remains strong, as do the hydrocarbon related projects. And perhaps as an indication of a future growth area, two new projects in carbon nanotube composites have begun this year, based on an LDRD ER that finished in 2008. As the STC regroups and shifts its focus, we look forward to continuing our work in support of the energy security component of the Lab mission.

—*Superconductivity Technology Center Leader Ken Marken*